

CLEAN-CHAR PROCESS

By

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U. S. Steel currently uses about 25 million tons of coal per year for production of the coke for our blast-furnace operations. In addition, we are one of the nation's leading holders of coal reserves. Accordingly, we have had a sustained interest in research and development work in coal, cokemaking, and coal utilization over the years. This interest was formalized in 1950 with the establishment of a coal and coke research and development group in U. S. Steel's Research Laboratory. The activities of that group have included the development of improved mining techniques, the development of new and improved coal and coke testing methods, the development and calibration of experimental coke ovens that would simulate the performance of commercial ovens with reference to the quality of coke produced, studies on coal beneficiation and the development of improved coking blends and procedures, the development of petrographic procedures for characterizing coals and calculating suitable coking blends from these coals, and the investigation of methods for more effective utilization of our coal reserves.

With regard to this latter area of activity, in the early '60's, our management charged us with the responsibility for developing a means for utilizing U. S. Steel's extensive Illinois coal reserves. These coal reserves are high in sulfur and ash content and are normally not considered suitable for making coke by the coke-oven procedure. A number of coal-conversion processes were explored. However, the

program made little progress because of the unattractive economics associated with coal-conversion processes at that time. It was not until the late '60's that the impending energy crisis was beginning to appear, together with the ecological factors that were increasing the cost of coke produced in coke ovens. As a result of these two developments, interest was renewed in conversion of the Illinois coal to coke by a method which would have economic and ecological advantages over the coke-oven route. Accordingly, the Clean-Coke Process was developed and evaluated in bench-scale equipment. This evaluation indicated that the Process would be technically and economically feasible. Because the project offered promise of interest to the chemical industry as well as the steel industry as a whole and had attractive ecological and energy and resource conservation features, it appeared that Government support was warranted. Accordingly, an unsolicited proposal was prepared and submitted to the Office of Coal Research. The program was accepted by OCR and is now in its second year of development. This program was reported in detail at the Philadelphia AIChE meeting last November and therefore will only be briefly discussed today to provide suitable background for the subject of the current paper.

Basically, the Process provides for obtaining about 34 percent of the coal fed to the process as metallurgical coke pellets—a fairly high-value carbonaceous product, generally considered to be worth about \$35 to \$40/ton or \$1.40 to \$1.60 per million Btu. The removal of this amount of high-carbon-containing product then results in a much more

favorable hydrogen-to-carbon ratio in the remaining material, such that about 18 percent of the coal is recovered as chemical feedstocks valued at an average of \$120/ton.

The Process (Figure 1) is most simply characterized as a unique combination of low-temperature carbonization and hydrogenation processes, integrated in a manner that permits optimum utilization of energy and materials. The coal fed to the Process, after beneficiation and sizing in a coal-preparation plant, is split into two fractions. Part of the coal is processed through a carbonization unit where it is devolatilized and partially desulfurized to produce the char that serves as the base material for production of the metallurgical coke. The second portion of the coal is slurried with a process-derived carrier oil and is hydrogenated to convert most of the coal to liquids. Liquid products from both carbonization and hydrogenation are composited and processed through a central liquids-treatment unit. In this unit, the liquids are processed into low-sulfur liquid fuels, chemical feedstocks, and three oil fractions that are recycled to other areas of the process. One of these recycle fractions is used primarily as a carrier oil for the hydrogenation reaction. A second recycle oil is sent to the carbonizer where it is converted to pitch coke. The pitch coke and char mixture is blended with the third recycle oil that serves as a binder, and the mixture is formed into pellets in the coke-preparation unit. These pellets are subsequently baked to produce a formed

metallurgical coke with strength properties equivalent to blast-furnace coke made by a conventional coking operation. The coke-preparation cycle, from char production to final coke, is carried out in a closed system with the off-vapors collected and returned to the process. Thus, no significant emissions of volatile matter occur during these operations, and atmospheric pollution is practically nonexistent. Gaseous products from all operations are processed through a common system to provide chemical feedstocks, low-sulfur gaseous fuels, and hydrogen for recycle to hydrogenation and liquids treatment.

The objective of the current Clean-Coke Program is to develop design information for a pilot plant that will process up to 10 tons of coal per hour.

In view of the recent high level of interest on clean energy, and especially on clean power-plant and industrial fuels, the technology of the Clean-Coke Process was studied to determine whether it might be applicable to the industrial fuel problem. The Environmental Protection Agency has suggested as a guideline that coal containing the equivalent of 0.6 lb of sulfur per million Btu be utilized to achieve the 1975 ambient air criteria. This is equivalent to 0.7 percent sulfur in coal having a heating value of 12,000 Btu/lb, and would mean only the Western coals and some limited tonnages of West Virginia, Kentucky, and Alabama coals would be suitable for use. In view of the fact that the carbonization-desulfurization portion of the Clean-Coke Process converts 2.0 percent sulfur coal

into char containing 0.4 to 0.6 percent sulfur, it is apparent that this operation could be utilized for production of an ecologically acceptable boiler fuel. Accordingly, this approach—called the "Clean-Char" Process—was further studied for technical and economical feasibility.

The proposed Clean-Char Process is illustrated in Figure 2. In this process, the carbonizer feed coal, after pulverization and sizing to minus 1/8 inch by plus 100 mesh, is first fed to a fluid-bed preheater where it is dried and preheated to about 400 F, utilizing stack gases from the main carbonizer heater which are boosted in temperature by passing them through an additional furnace. The off-gases from the preheater, after removal of particulate matter in a cyclone, go to a stack. The preheated coal then enters the fluid-bed carbonizer where it is heated by the fluidizing gas and carbonized at temperatures from 1200 F to 1400 F at about 90 to 100 psi pressure. By maintaining the hydrogen content at about 33 percent and the sulfur content at a low level, the fluidizing gas serves to simultaneously carbonize and desulfurize the coal fed to the carbonizer. After separation of particulates, the carbonizer off-gas is cooled in three steps and desulfurized to provide the gas for recycle to the carbonizer and the surplus gas which is suitable for use as a low-sulfur, medium Btu (about 636 Btu/SCF) fuel gas. The condensed tars and moisture are separated from the system and the water sent to a waste-treatment unit. The tar contains about 1.0 to 1.2 percent sulfur and therefore would not be suitable for fuel, in view of the 0.7 percent sulfur limitation. However, there are three possibilities for its use: (1) It could be sold to a refinery

for processing; (2) it could be burned along with the char. (Because the weight of the char amounts to about 3.5 times that of the tar, the blend of 0.5 percent sulfur char and 1.2 percent sulfur tar would have a sulfur content of only 0.66 percent), and (3) it could be recycled to the carbonizer and thus be converted to fluid coke and gas. The material balance information is summarized in Figure 3. Properties of the coal and char are given in Table I and the composition and calculated heating value of the gas are given in Table II.

An economic evaluation of the process was then made to enable the cost of the Clean Char to be compared with other alternatives. In the evaluation, capital and operating costs have been developed for a plant to supply a 1000 megawatt (MW) power plant with a 60 percent load factor. This would require 38,970,000 million (MM) Btu (or 1,457,041 tons) of char plus 14,100,000 MM Btu (or 416,713 tons) of tar. Thus, the material balance for the economic study corresponds to that of Figure 3. Economics have been evaluated using "The Office of Coal Research Tentative Standard for Cost Estimating of Investor-Owned Plants for Producing Pipeline Gas from Coal," (June 4, 1965).

Table III presents a summary of the estimated items comprising the total capital investment. Total fixed investment, including battery limits, utilities, offsites, and construction loan interest is \$90.3 million. The addition of \$5.6 million working capital results in a total capital investment of \$95.9 million.

Table IV shows estimated annual operating expenses. By-product credits of \$10.3 million include a \$9.35 million fuel

gas credit, an \$835,000 sulfur credit, a \$97,000 steam credit, and a \$21,200 ammonia credit. These credits reduce operating expenses to a net \$27.86 million.

Table V presents an economic summary. The OCR standard includes provision for construction loan and working capital, 20-year straightline depreciation, and a 65-35 debt-to-equity ratio. The standard guarantees a gross return of 7 percent of the rate base (total fixed investment declining on a 20-year basis plus working capital). Total revenue is calculated by adding net operating expenses (including 5 percent interest on unpaid debt), gross return, and income tax. The 65 percent debt portion of the investment is paid off in equal installments over a 20-year period. Selling price, which is total revenue divided by annual through-put, varies from year to year. The average price for a 20-year period is the reported value. Applying the OCR standard, the revenue requirement for char and tar fuels is \$0.63 per MM Btu.

Coal cost is the major cost element. Figure 4 shows the effect of coal cost on fuel selling price. A \$2.00/ton increase in coal cost increases solid and liquid fuel price by about \$0.107 per MM Btu (including operating-cost contingency).

In view of the fact that there are limited supplies of low-sulfur coals in the central and eastern United States and that low-sulfur oil is becoming scarce and expensive, many utilities and industrial plants are considering stack-gas scrubbing to enable them to use higher sulfur coals and still comply with emission standards. It is our

understanding that there is no commercial stack-gas scrubbing unit operating satisfactorily and that recent costs for stack-gas scrubbing have been estimated at \$50 to \$90 capital per KW and \$0.80 to \$0.95 per MM Btu total fuel cost (coal cost plus scrubbing cost). It would therefore appear that the Clean-Char Process with its \$90 per KW capital plant investment and \$0.63 per MM Btu total fuel cost should be of interest.

Table I

Properties of Coal and Char

	<u>Percent by Weight</u>	
	<u>Coal</u>	<u>Char</u>
H ₂ O	8.51	--
Ash	5.17	6.57
<u>Elemental Analysis</u>		
Carbon	68.77	86.73
Hydrogen	4.79	2.47
Nitrogen	1.24	1.48
Oxygen	9.73	2.28
Sulfur	1.79	0.47
Heating value, Btu/lb		13,373

Table II

Properties of Fuel GasComposition, percent by Volume

Hydrogen	33.52
Methane	37.06
Ethylene	12.95
Ethane	2.87
C ₃ and C ₄	1.60
Carbon Monoxide	10.66
Carbon Dioxide	.85
Moisture	<u>.49</u>
	100.00

Heating Value 636 Btu/SCF

Table III

Investment Summary

<u>Section</u>	<u>Title</u>	<u>Cost, \$MM</u>
100	Carbonization	52.7 (a)
200	Gas Cleaning	12.4 (b)
300	Claus	2.0 (c)
400	Tar Handling	1.3 (d)
500	Utilities and Waste Water	4.2 (e)
600	Off site facilities	<u>7.3</u> (f)
	Subtotal	79.9 (g)
	Contractor's Overhead and Profit	<u>6.1</u> (h)
	Subtotal	86.0 (i)
	Interest During Construction (5% of (i))	<u>4.3</u> (j)
	TOTAL FIXED INVESTMENT	90.3 (k)
	<u>Working Capital</u>	
	30 days coal inventory	2.0 (l)
	30 days catalyst, etc., inventory	- (m)
	Accounts receivable	<u>3.6</u> (n)
	Total working capital	5.6 (o)
	TOTAL CAPITAL INVESTMENT	95.9 (p)

Table IV

<u>Operating Expense</u>	
	<u>\$/Year</u>
Raw Material (Coal) @ \$8.00/ton	22,372,300 (A)
Utilities	2,124,700 (B)
Direct Operating Labor @ \$5.75/hr	891,500 (C)
Maintenance (3% of (g))	2,397,000 (D)
Supplies (15% of (D))	359,600 (E)
Supervision (10% of (C))	89,200 (F)
Payroll Overhead (10% of (C) + (F))	98,100 (G)
General Overhead (50% of (C)+(F)+(D)+(E))	<u>1,868,700 (H)</u>
Plant Operating Expenses Subtotal	30,201,100 (I)
Depreciation (5% of TOTAL FIXED INVESTMENT)	4,515,000 (J)
Local Taxes and Insurance (3% of TOTAL FIXED INVESTMENT)	<u>2,709,000 (K)</u>
Subtotal	37,425,100 (L)
Contingencies (2% of (L))	<u>748,500 (M)</u>
TOTAL OPERATING EXPENSE	38,173,600 (N)
By-Product Credits	<u>10,311,600</u>
NET OPERATING EXPENSE	27,862,000

Table V

Economic Summary¹⁾

Annual Production	38,971,000 MM Btu Char	
	<u>14,099,000</u> MM Btu Liquids	
	53,070,000 MM Btu Total	
Plant Investment, ²⁾ MM\$		90.3
Working Capital, MM\$		<u>5.6</u>
Total Capital, MM\$		95.9
<u>Costs, \$MM Btu</u>		
Gross Raw Materials	0.4216	
By-Product Credits ³⁾	<u>0.1943</u>	
Net Raw Materials		0.2273
Utilities	0.0400	
Labor	0.0203	
Maintenance and Supplies	0.0520	
General Overhead	0.0352	
Depreciation, Taxes, Insurance	0.1360	
Contingencies	<u>0.0141</u>	
Net Operating Expense		0.2976
Profit, Taxes, Interest ⁴⁾	0.1060	<u>0.1060</u>
SELLING PRICE, \$/MM Btu		0.6309

¹⁾ February 1973 dollars.

²⁾ Includes construction load interest.

³⁾ Includes 9,358,000 MM Btu of gas credited at \$1.00/MM Btu

⁴⁾ Interest at 5 percent annual rate.

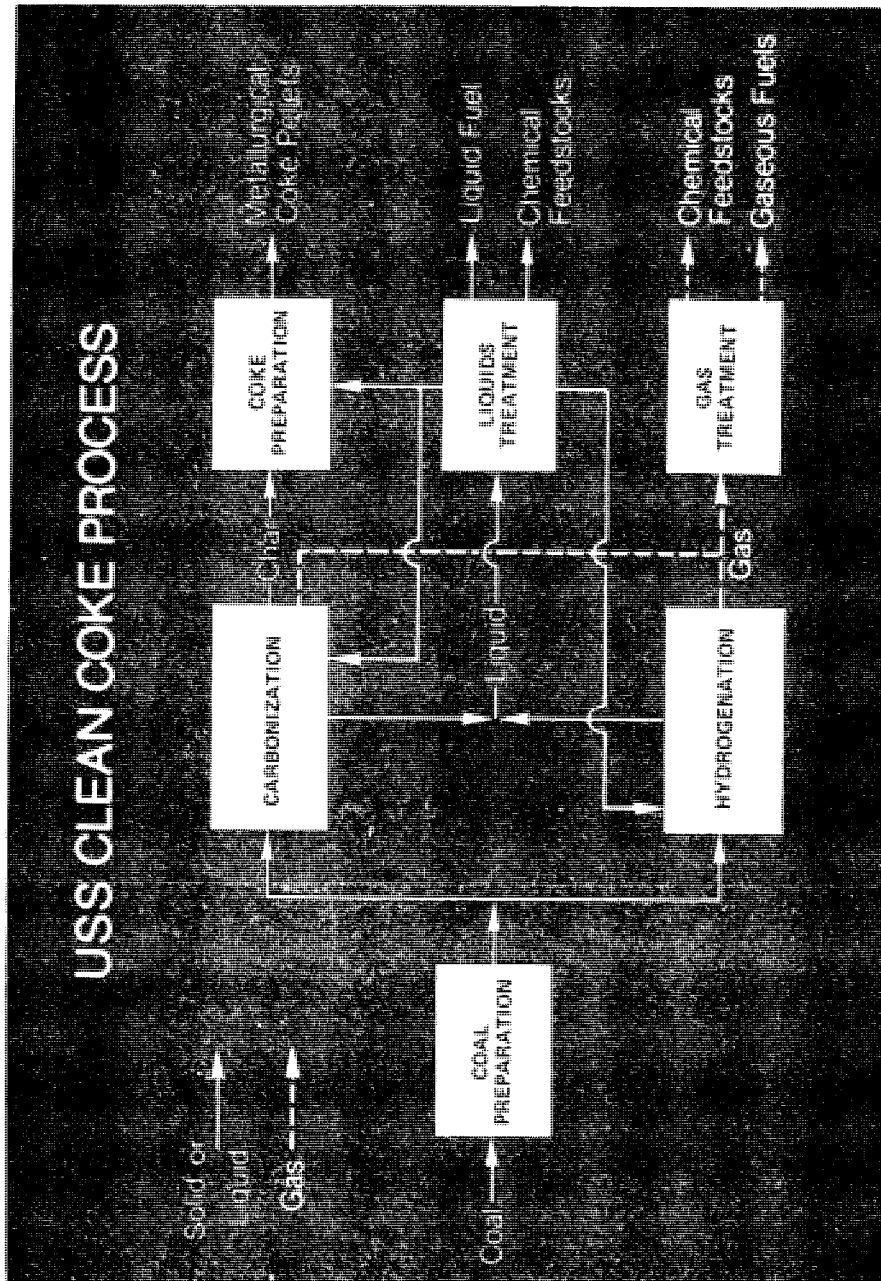


Figure 1.

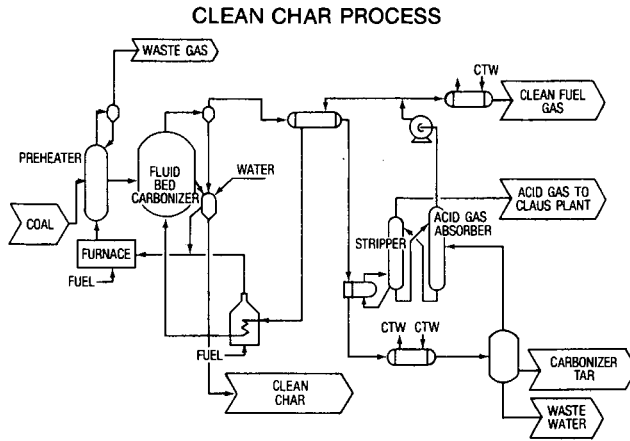


Figure 2.

CLEAN-CHAR PROCESS—MATERIAL BALANCE

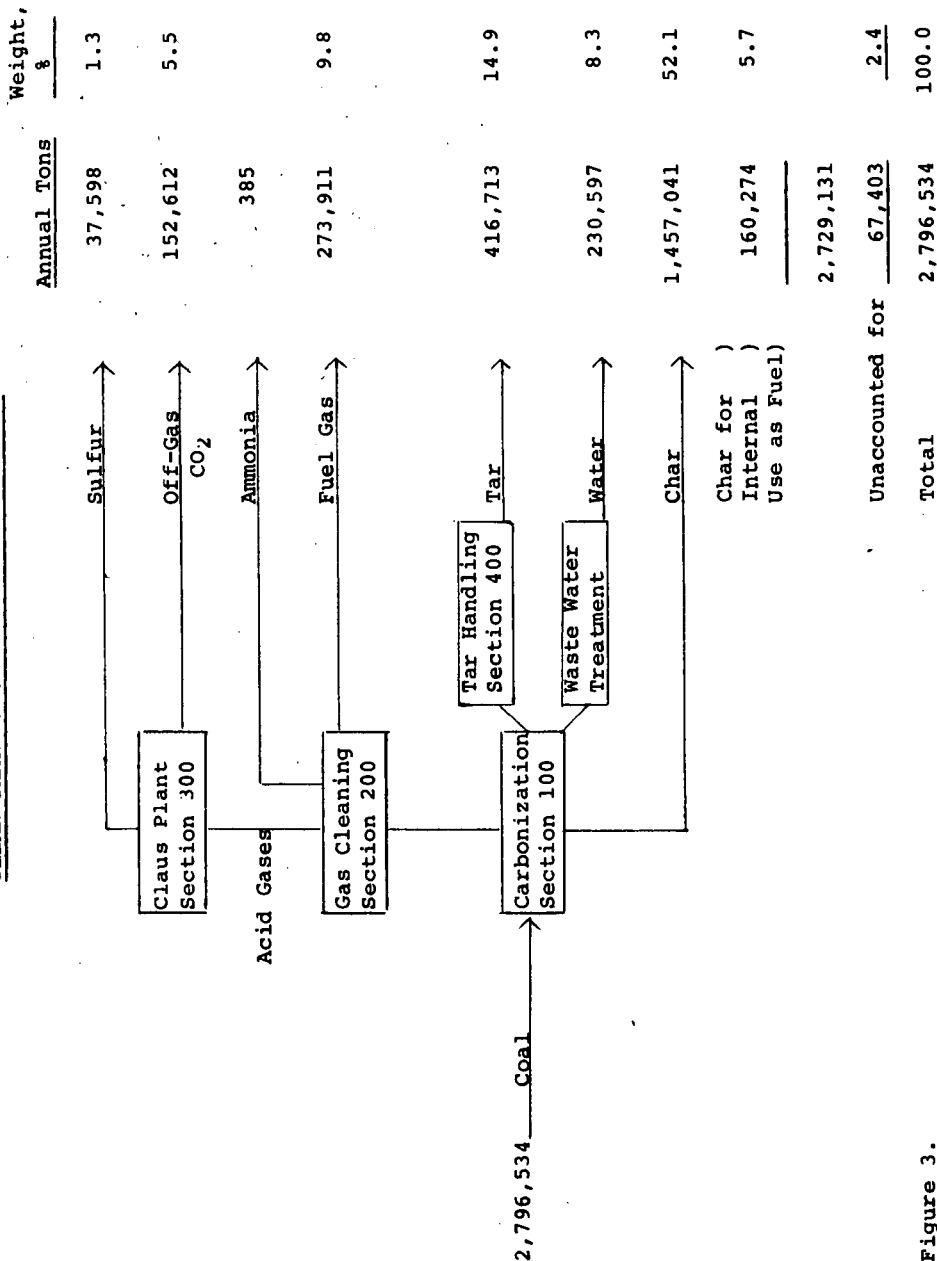


Figure 3.

\$90,300,000 Total Fixed Investment
 38,971,000 MM Btu Char
 14,099,000 MM Btu Tar
 53,070,000 MM Btu Total
 9,358,000 MM Btu Gas as By-Product
 at \$1.00/MM Btu

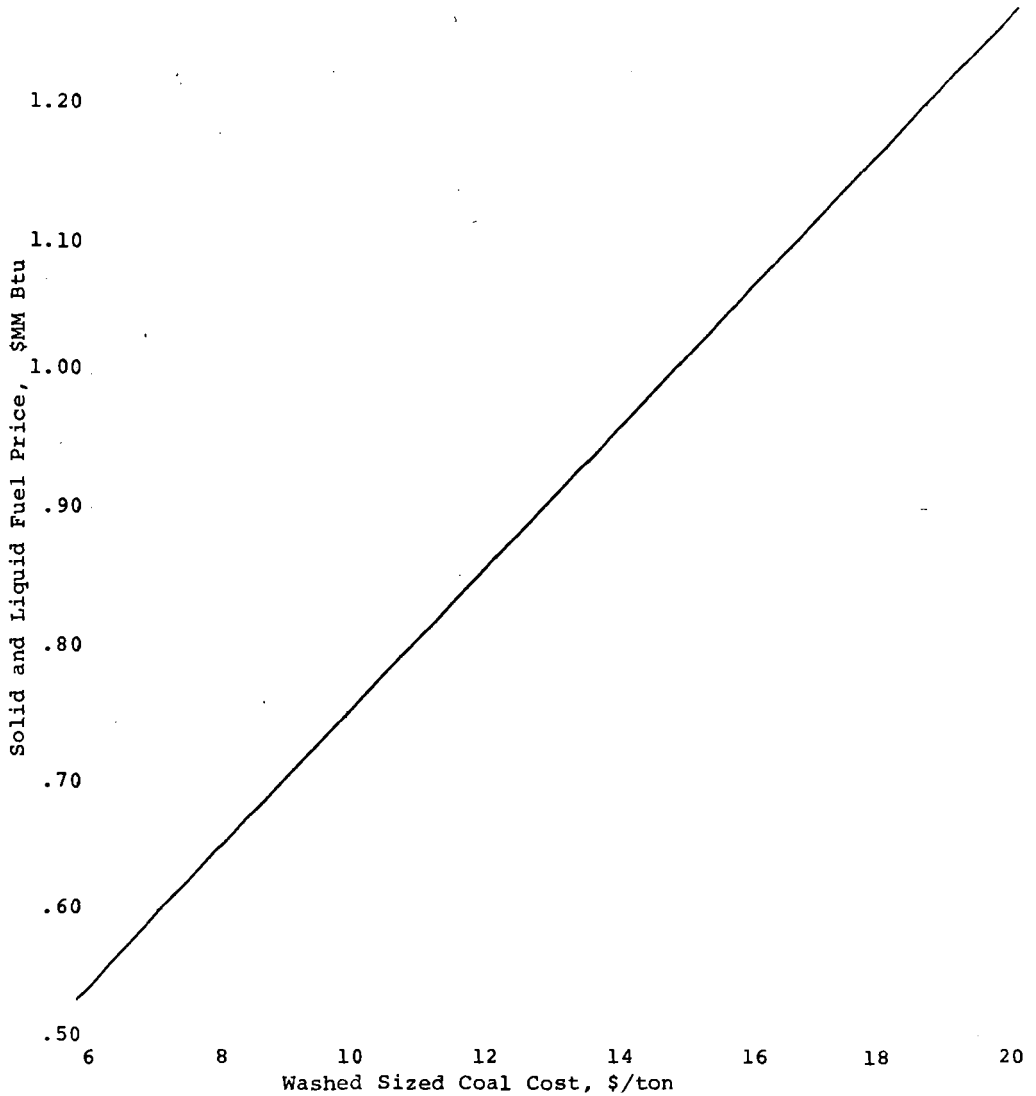


Figure 4. EFFECT OF COAL COST ON SOLID AND LIQUID FUEL PRICE USING OCR STANDARD

AN IMPROVED TECHNIQUE FOR THE
HYDRODESULFURIZATION OF COAL CHARs

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INTRODUCTION

The sulfur content of many coals is too high to comply with the EPA standard for power plant fuels. The current alternatives for utilizing coal as a fuel include either complete gasification of the coal with the sulfur removal effected by conventional gas treatment, or direct combustion of the coal with stack gas scrubbing.

In a carbonization process such as the patented GR&D flash pyrolysis process, the coal is converted into char. Although the sulfur content of the chars is normally less than that of the parent coals, most chars must still be treated to reduce the sulfur content to comply with EPA standards. We have developed an improved hydrodesulfurization process that accomplishes the required sulfur reduction. We propose that this process is more advantageous than the current alternatives for utilizing the coal directly.

Earlier work conducted by Consolidation Coal Company (1, 2) and by FMC Corporation (3, 4) demonstrated that hydrogen treatment of the char at elevated temperatures is effective in the removal of sulfur. However, the presence of the hydrogen sulfide product gas strongly inhibited the removal of additional sulfur. Either a large excess flow of hydrogen had to be maintained or the introduction of a hydrogen sulfide acceptor such as dolomite was necessary (3,4, 5). However, the utilization of an acceptor presents several difficult problems which include separation from the char, regeneration, and loss of acceptor activity. Obviously, the direct treatment of the char with hydrogen to remove sulfur would be more practical if the effects of the hydrogen sulfide inhibition could be reduced. Our work shows that the effect of the hydrogen sulfide inhibition can be minimized by pretreating the char with acid. Hydrogen sulfide inhibition isotherms (char sulfur contents at extended residence times) indicated that a significantly greater concentration of hydrogen sulfide is allowable for the acid-treated chars than for the untreated chars. This represents a significant reduction in both the capital and operating costs of a commercial hydrodesulfurization facility by

allowing a reduction in the hydrogen throughput. For a counter-current hydrosulfurization system with three stages, the hydrogen requirement for acid-treated char is only 12% of that for the untreated char.

EXPERIMENTAL

Apparatus

The experimental apparatus utilized in the hydrogen treatment of the char (Figure 1) consists of a 4' x 19mm I-D quartz reactor which is inserted in a Hevi Duty electric furnace. The ends of the reactor are sealed with Teflon gaskets and are cooled by water circulating through copper coils. The gas flow to the reactor is controlled by means of a rotameter, and the system pressure is maintained by a back-pressure regulator. Gas flow calibrations were obtained with a wet-test meter.

The reactor was packed with ceramic burl saddles up to the middle of the hot zone, and a Kaowool plug was positioned on top of the saddles to prevent char from falling through the reactor. In addition, a Kaowool plug was positioned at the top of the hot zone to prevent elutriation of the char particles.

Procedure

Helium gas flow at the reaction pressure was maintained during reactor start-up. The temperature was established by an Alnor controller in conjunction with a chromel-alumel thermocouple positioned externally to the reactor. After sufficient saturation time was allowed at the desired temperature, hydrogen or a mixture of hydrogen and hydrogen sulfide from calibrated cylinders was introduced to the reactor for the desired reaction time. The system was then purged with helium, and the temperature was allowed to return to ambient.

Char Preparation

Chars were prepared by carbonizing several selected coals under nitrogen at elevated temperatures. These coals included a high volatile C bituminous coal from West Kentucky and a high sulfur bituminous coal from Illinois. Chars were produced both from run-of-mine coals and from samples which had been physically beneficiated by a sink/float technique prior to the carbonization. The chars

were ground and screened to the desired particle size. The chars to be acid-treated were leached with 80°C hydrochloric acid for approximately five minutes. After the acid leach, the char was washed with water until the water was free of chloride ion as determined by the silver nitrate test.

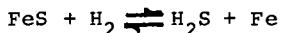
Chemical Analyses

A complete sulfur analysis was performed on the reactant and product chars. The total char sulfur was measured by the Eschka method. The sulfide, sulfate, and pyritic sulfur forms were also measured. An ultimate analysis was also performed to allow estimation of the char combustion heats.

The metals in the char ash were analyzed by either emission spectra or by atomic absorption. Fe^{+2} was measured by leaching the char with a solution of HF and H_2SO_4 followed by titration with KMnO_4 . Fe^0 was measured by reacting the char with a solution of Hg_2Cl_2 followed by atomic absorption of the final solution. Very little Fe^0 was observed in any of the tests. Fe^{+3} was determined by difference.

DISCUSSION

Previous work has demonstrated that the presence of hydrogen sulfide greatly inhibits the hydrodesulfurization of char. In addition, inhibition isotherms were presented that show plateaus of sulfur in the char at low concentrations of hydrogen sulfide in the treatment gas. (2, 6) These plateaus were attributed to the equilibrium in the reduction of iron sulfide.



The presence of calcium sulfide, which is irreducible by hydrogen treatment, was also noted.

Although the reaction of carbonaceous materials with hydrogen and hydrogen sulfide mixtures is reversible, the reaction is not a true equilibrium process (2). The type of carbonaceous material, the type of pretreatment, and the temperature and time of treatment all affect the extent of the reaction. Since both inorganic and organic sulfur forms exist in the char, different methods must be employed to completely remove both forms. We chose to study the effects of an acid pretreatment to remove inorganic sulfur and a subsequent hydrogen treatment to remove the organic sulfur. However, the additional removal of the iron and calcium hydrodesulfurization reaction.

Hydrogen Sulfide Inhibition Isotherms

The hydrogen sulfide inhibition isotherms at 1600°F and 50 psig for three chars prepared from West Kentucky Coal are shown in Figure 2. The three char samples were prepared by carbonizing the run-of-mine coal, floating the coal in a 1.55 s.g. ZnCl_2 solution prior to carbonization, and by acid treating the char from the floated coal. The chars were ground and screened to a -80 +270 mesh particle size. The char samples were then hydrogen treated for approximately 2-1/2 hours. The char from the run-of-mine coal exhibited the greatest hydrogen sulfide inhibition. Although the char from the floated coal compares favorably with the acid-treated char in the limit of pure hydrogen, the acid-treated char exhibited the least hydrogen sulfide inhibition.

Hydrogen sulfide inhibition isotherms for three similar chars prepared from the Illinois coal are compared with the isotherms for the West Kentucky coal chars in Figure 3. Although the hydrogen sulfide inhibition is in general slightly less severe for the Illinois coal chars, the floating and acid treating operations also reduce the severity of the hydrogen sulfide inhibition for these chars. However, the inhibition isotherms for the acid-treated chars from the West Kentucky and Illinois coals are practically identical.

The effect of the iron and calcium content of the chars on the inhibition isotherms is apparent in Table I. The quantity of iron and calcium is highest in both the West Kentucky and Illinois run-of-mine chars. The higher iron content of the West Kentucky char may be responsible for the slightly more severe inhibition isotherms shown in Figure 2. An intermediate quantity of iron and calcium is contained in the two chars from the floated coals. The higher iron content of the West Kentucky char again corresponds to a slightly more severe inhibition isotherm. The lowest quantity of iron and calcium is contained in the acid-treated chars. These chars also have the least severe inhibition isotherms.

Acid Treatment

Hydrochloric acid was utilized in the preparation of the acid-treated chars in Table I. Although significant quantities of ash were removed by floating the coal, the char from the floated coal still contained appreciable quantities of iron and calcium. The final reduction in the quantities of iron and calcium was accomplished by the acid treatment. The char ash also contains large quantities of silicon, aluminum, potassium, and sodium, but these were only slightly affected by the acid treatment.

Some sulfur reduction is also accomplished in the physical beneficiation step by the removal of pyrite. Almost all of the remaining pyrite sulfur is converted to FeS during carbonization. This sulfur is removed by the acid treatment along with additional quantities of Fe^{+2} , Fe^{+3} , and calcium. The total sulfur in the char of the beneficiated West Kentucky coal is reduced from 1.90 to 1.34% by the acid treatment, which is in very close agreement with the measured reduction in sulfide sulfur from 0.57 to 0.10%.

The type of mineral acid utilized in the acid treatment does not appear to affect the final desulfurization. The inhibition isotherms for sulfuric acid-treated char were identical to those chars treated with hydrochloric acid (Figure 2).

Finally, the beneficiation operation is not essential to the final desulfurization. The inhibition isotherms for acid-treated chars from the run-of-mine coals were identical to those chars which were prepared from floated coals. The advantage of the beneficiation operation appears to be in the initial removal of most of the pyritic sulfur and in a reduction of the quantity of acid consumed in the char treatment.

Optimum Desulfurization Temperatures

Chars prepared at low temperatures and short residence times might be expected to have a more labile form of organic sulfur than chars prepared at high temperatures and long residence times. The more severe conditions would increase the probability of thermally fixing the organic sulfur, which would be stable in the presence of hydrogen (7). Since the chars in this study were prepared by carbonization of the coal at the anticipated desulfurization temperature for over two hours, any expected thermal fixing of char sulfur should have occurred.

The optimum desulfurization temperature for the chars from the West Kentucky coal was found to be between 1700 and 1800°F as illustrated in Figure 4. This same optimum temperature occurred for all coal and char pretreatment methods.

Much lower optimum desulfurization temperatures of 1300 and 1470°F had been found in the desulfurization of petroleum coke with hydrogen (8) and butagas, a coke-oven gas which is predominately butane (9). The latter optimum was attributed to the sintering of the coke particle with a subsequent loss of available surface area.

However, no evidence of sintering was observed in the case of the coal chars.

Hydrodesulfurization Kinetics

Although most of the screening of variables has been accomplished in terms of the hydrogen sulfide inhibition isotherm, the hydrodesulfurization of char is not a true equilibrium process. An adequate description of the kinetics of hydrodesulfurization is essential if the design of commercial equipment is anticipated. We are currently undertaking such a kinetic study.

The kinetic data for the hydrodesulfurization of floated char and acid-treated char from the West Kentucky coal at 1700°F and 50 psig is shown in Figure 5. These chars were ground to a -200 mesh particle size. Rate data are shown for various compositions of hydrogen and hydrogen sulfide reactant.

Although the initial sulfur content of the acid-treated char is lower than that for the floated char, the initial disappearance rates of sulfur for the two chars in contact with pure hydrogen are quite similar. In contrast, the disappearance rate of sulfur for the acid-treated char in contact with even a small quantity of hydrogen sulfide is faster than that for the floated char. In addition, these data at long residence times indicate much lower final sulfur contents for the acid-treated chars.

The mechanism of hydrodesulfurization appears to be quite complex. For example, the removal of the first fifty percent of the sulfur in the acid-treated char can be described by first order kinetics while the remainder appears to follow a zero order reaction. These data cannot be explained by a hydrogen sulfide reverse reaction. If the flow rate of hydrogen were maintained sufficiently low, the sulfur released by the hydrodesulfurization might become more firmly attached to the char. However, tests conducted at one-half the normal experimental hydrogen flow demonstrated that the effect of a reverse reaction was not important in this study. The results of these tests are indicated in Table II.

The hydrodesulfurization kinetics might be explained by a rapid evolution of sulfur on the char surface followed by the slower removal of sulfur in the char interior. Since similar rates were

obtained from tests conducted at 1600 and 1700°F, the hydrodesulfurization kinetics is probably not controlled by a chemical reaction mechanism. Also, tests conducted on a -60 +80 mesh char were not appreciably different from similar tests conducted on the same char which was ground to a -200 mesh particle size. These data are in accordance with a pore diffusion mechanism (3).

Counter-current Hydrodesulfurization

A significant reduction in the hydrogen requirement of any commercial hydrodesulfurization process can be realized by counter-current staging. However large throughputs of hydrogen are still required if untreated char is to comply with EPA standards. In contrast, the acid-treated chars can be handled quite effectively by the counter-current process.

Based on calculated heats of combustion of 12,000 and 13,000 Btu/lb char for floated char and acid-treated char and the EPA standard for 1.2 lb SO₂/MM Btu (10), final char sulfur contents of 0.72 and 0.78% would meet the criterion for the West Kentucky coal. If the floated char were to be desulfurized in a single stage, 73 pounds of hydrogen would be required for every 100 pounds of char. If the floated char were to be desulfurized in three counter-current stages, the hydrogen requirement would be reduced to 8.5 pounds. However, only 1.0 pounds of hydrogen is required to desulfurize 100 pounds of acid-treated char in three counter-current stages. In the multistage process, the hydrogen requirement for acid-treated char is only 12% as high as that for floated char.

Conclusions

The effectiveness of the hydrodesulfurization process for coal chars is significantly improved, in turn, by the physical beneficiation of the parent coal and by the acid treatment of the product char. These processes have been effective in the removal of iron and calcium constituents which appear to contribute to the severity of the hydrogen sulfide inhibition. The acid treatment is particularly advantageous in that both the iron and calcium contents of the char are reduced well below that of the floated coal char. In addition, the remaining ash constituents which are not removed by the coal beneficiation treatment are not affected by the acid treatment. Thus, the consumption of the acid is minimized.

A significant reduction in the hydrogen requirement of the commercial hydrodesulfurization process can be realized by counter-

current staging. An additional significant reduction is accomplished by acid treatment of the char. In the multistage process, the hydrogen treatment for acid-treated char from the West Kentucky coal is only 12% of that required for the untreated char from the beneficiated coal.

The optimum desulfurization temperature which was determined for the chars of the West Kentucky coal used in this study appears to be in the range of 1700 to 1800°F. However, this optimum temperature may vary with the method of char preparation.

Preliminary kinetics studies indicate that the acid treatment technique reduces the effect of hydrogen sulfide inhibition in the disappearance of the char sulfur.

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Table IChar Analysis for Ash, Calcium, and Iron

<u>Char</u>	<u>Ash</u> <u>Wt. %</u>	<u>Ca</u> <u>Wt. %</u>	<u>Fe</u> <u>Wt. %</u>	<u>Fe⁺²</u> <u>Wt. %</u>	<u>Fe⁺³</u> <u>Wt. %</u>
West Kentucky Run-of-Mine Carbonized at 1600°F	23.0	0.9	2.8	1.3	1.5
West Kentucky 1.55 S.G. Float Carbonized at 1600°F	10.9	0.1	1.13	0.67	0.46
West Kentucky 1.55 S.G. Float Carbonized at 1600°F and acid-treated	9.5	0.06	0.32	0.03	0.29
Illinois Run-of-Mine Carbonized at 1600°F	16.06	1.01	1.75	1.35	0.40
Illinois 1.55 S.G. Float Carbonized at 1600°F	9.93	0.13	0.76	0.37	0.39
Illinois 1.55 S.G. Float Carbonized at 1600°F and acid-treated	9.33	0.08	0.27	0.005	0.27

Table IIEffect of Hydrogen Flow Rate on Desulfurization ofAcid-Treated Char from West Kentucky Coal at1700°F and 50 psig

<u>Flow Rate</u> <u>SCFM</u>	<u>Time</u> <u>Min.</u>	<u>Char Sulfur</u> <u>Wt %</u>	<u>Superficial Velocity</u> <u>ft/sec</u>
0.030	5	0.92	0.151
0.015	5	0.90	0.076
0.030	15	0.79	0.151
0.015	15	0.77	0.076

FIGURE 1
EXPERIMENTAL APPARATUS

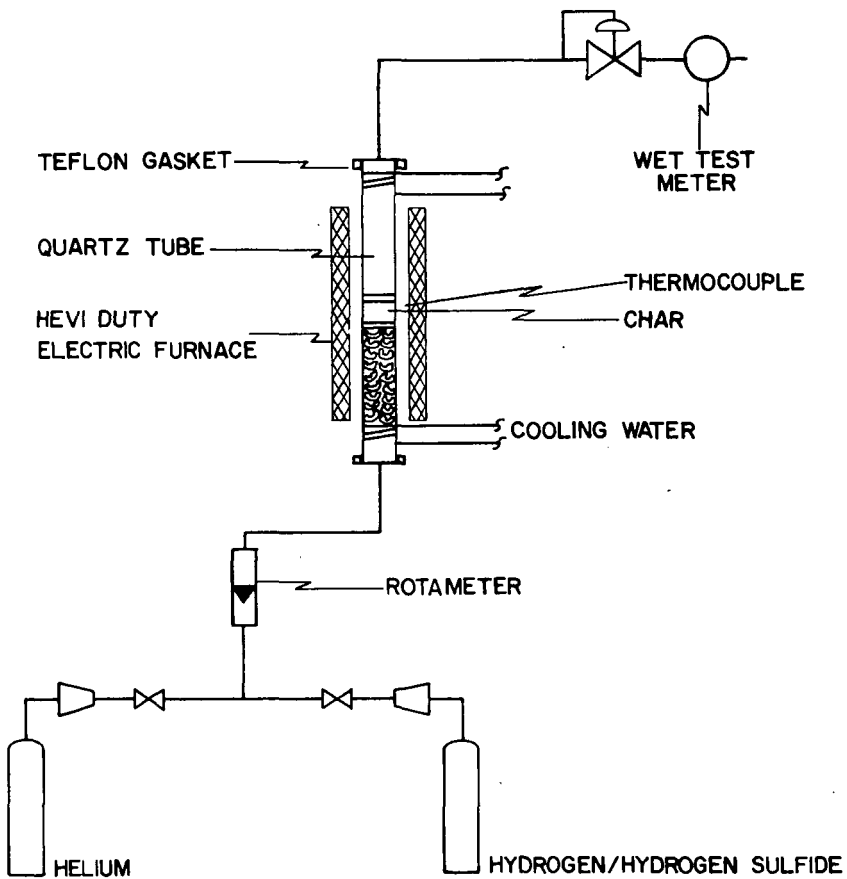


FIGURE 2
HYDROGEN SULFIDE INHIBITION ISOTHERM FOR WEST KENTUCKY
COAL CHAR

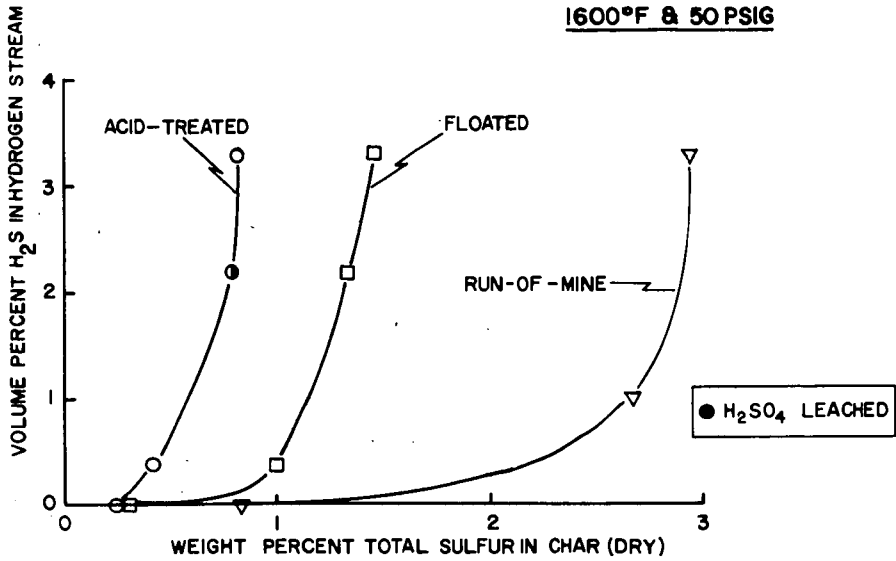


FIGURE 3
COMPARISON OF WEST KENTUCKY AND ILLINOIS COAL CHARS

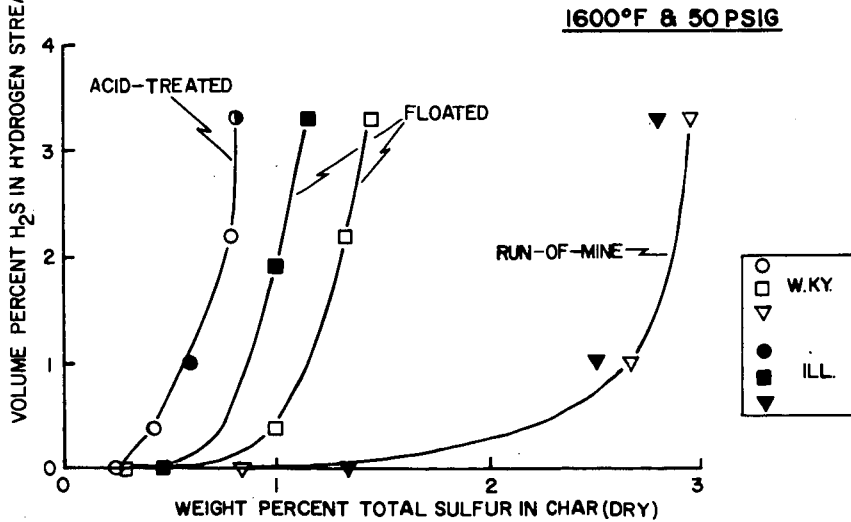
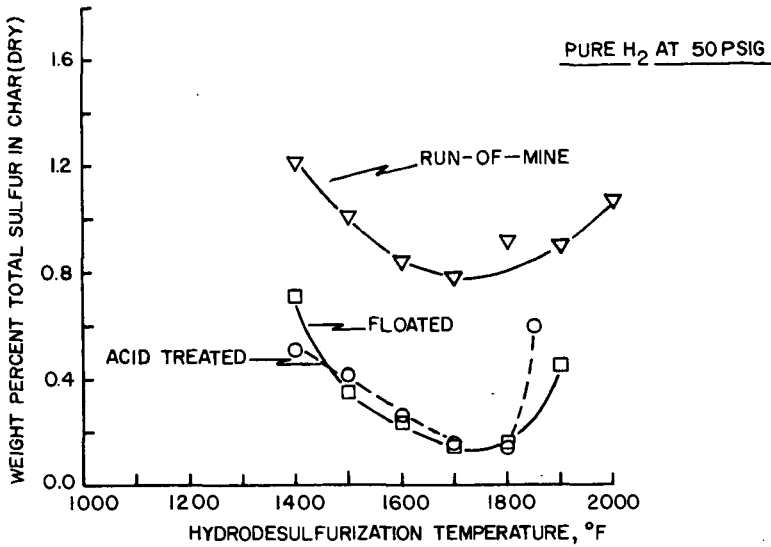
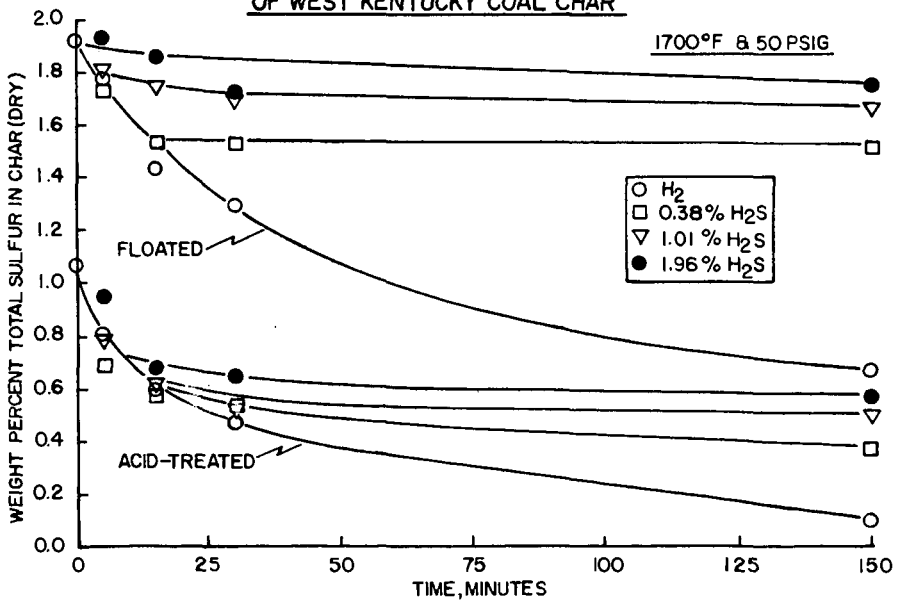


FIGURE 4**VARIATION OF CHAR SULFUR WITH TEMPERATURE FOR WEST KENTUCKY COAL CHAR****FIGURE 5**
HYDRODESULFURIZATION KINETICS
OF WEST KENTUCKY COAL CHAR

CHEMICAL DESULFURIZATION OF COAL by E. P. Stambaugh, Battelle,
Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

Coal is the major source of energy now available to the United States. In fact, within the border of the United States, there is more energy in the form of coal than in all of the other combined sources of fossil fuel. Though a major energy source, coal is recognized as a major source of atmospheric pollution. In the absence of controls other than tall stacks, the discharge of sulfur alone excluding the heavy metals in 1980 is estimated to be about 18 million tons. Sulfur emissions control from flue gases is about 75 percent efficient. Assuming all flues are controlled at the 75 percent level, sulfur emissions from power plants are estimated to be about 4.5 million tons (13.5 million tons of sulfur dioxide) by 1980. Chemical desulfurization of coal offers one potential solution to the sulfur emissions problem now facing the United States. Removal of all or a major portion of the sulfur from coal prior to combustion will result in a fuel which can be used with a low atmospheric pollution potential. The feasibility of producing low sulfur coal by chemical desulfurization has been established in laboratory scale experiments. Heating a variety of coals in aqueous solutions at elevated temperatures and pressures extracts the pyritic sulfur and the sulfate sulfur along with a significant portion of the organic sulfur.

CHEMICAL DESULFURIZATION OF COAL TO MEET POLLUTION CONTROL STANDARDS

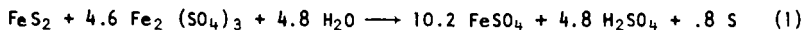
J.W. Hamersma, M.L. Kraft, W.P. Kendrick
and

R.A. Meyers

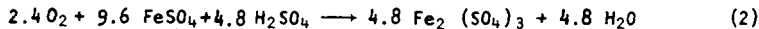
TRW Inc
One Space Park
Redondo Beach, California
90278

INTRODUCTION

The Meyers' Process is a new approach⁽¹⁾ for meeting federal and state sulfur oxide emission standards for coal-fired electric utilities. The process removes up to 80% of the sulfur from coal through chemical leaching of pyritic sulfur with aqueous ferric sulfate solutions at temperatures of 50°-130°C (eq 1).



The leaching agent is regenerated at similar temperatures using oxygen (eq 2).



and sulfur and iron sulfates are removed as reaction products. The selectivity for pyrite is high with little or no reaction of the reagents with the coal matrix being found for Appalachian coal.

Although only pyritic sulfur is removed (organic bound sulfur remains), the Meyers' Process has wide applicability for converting US coal reserves to a sulfur level consistent with governmental standards for sulfur emissions from power plants and industrial sources. Samples from coal mines in Montana, through Iowa, Illinois, Ohio, Pennsylvania, West Virginia and Kentucky, representing a wide range of US production and reserves have been desulfurized to meet these standards utilizing the Meyers' Process (Environmental Protection Agency Contract 68-02-0647). Physical cleaning has generally been unable to accomplish similar sulfur reductions for the coals tested without severe coal reject losses. Because of the relatively high pyritic sulfur and low organic sulfur contents of Appalachian coals (70% of current US coal production), the process appears to have major impact in this area.

The concept of chemically removing pyrites from coal has not heretofore been thought practical as a solution to the sulfur oxide air pollution problem, even though it is well known that pyrites may be oxidatively converted to soluble sulfates by strong oxidizing agents such as nitric acid, hydrogen peroxide or chlorine. These oxidizing agents are not seriously advanced as the bases of processes for lowering the sulfur content of coal as they also seriously oxidize the coal matrix. Furthermore, nitric acid nitrates coal and chlorine greatly increases the chlorine content of coal. A number of groups^(2,3) have investigated the use of hot alkali, but have abandoned this approach presumably because much of the input base reacts with coal silicates, aluminates and the organic matrix, causing excessive reagent and coal losses.

Aeration of coal in aqueous suspension has often been suggested for conversion of the pyritic sulfur content of coal to a soluble sulfate, as it is known that the mechanism of acid mine drainage involves slow conversion of pyrite to soluble sulfate. However, attempts to speed up this process under favorable conditions of air supply, temperature and fineness of coal have only resulted in a reduction of residence time to weeks or months rather than years⁽²⁾. Thus, it was not thought possible to devise a practical process for chemically removing or dissolving the pyritic sulfur content of coal.

Bench-scale tests of more than 200 ferric solution extractions and 50 leach solution regenerations have been performed to date (Environmental Protection Agency Contract EHSD 71-7) for the purpose of defining reaction kinetics. A typical expression for pyritic sulfur removal from (from Lower Kittanning coal) is⁽⁴⁾:

$$r_L = \frac{-d[W_p]}{dt} = K_L W_p^2 Y^2 = \text{wt of pyrite removed/100 wts of coal/hour} \quad (3)$$

where,

W_p = weight percent pyrite in coal,

Y = ferric ion to total iron weight ratio in leacher, and

$K_L = A_L \exp(-E_L/RT)$, a function of temperature and coal particle size,

and for ferric regeneration⁽⁴⁾:

$$r_R = \frac{-d[Fe^{+2}]}{dt} = K_R [O_2][Fe^{+2}]^2 = \text{moles of ferric ion regenerated per unit time,} \quad (4)$$

where,

$[O_2]$ = oxygen partial pressure in atmospheres,

$[Fe^{+2}]$ = ferrous ion concentration in moles/liter, and

$K_R = A_R \exp(-E_R/RT)$, a function of temperature only.

Experimental results for both Meyers' Process extraction and float sink testing (physical cleaning) of nineteen US coals are presented in the following section.

RESULTS

One-ton run-of-the-mine coal samples, representing at least one day's production were collected from each of 19 coal mines by Commercial Testing and Engineering Company of Chicago, Illinois. The coal mines were selected to provide information on a wide variety of coal beds and regions with special emphasis on the Appalachian Basin. The coal analysis summary (Table 1) shows that the coals range from sub-bituminous A through low volatile bituminous in rank, in total sulfur from 1.0 to 6.4%, and in pyritic sulfur from 0.3 to 5.2% w/w (dry, moisture-free basis).

TABLE 1
COAL ANALYSIS SUMMARY^a

Region	Seam	State	Mine	As Received Basis		Dry Forms of Sulfur, % w/w				Dry Proximate Analysis, % w/w			
				Rank	Moisture % w/w	Total	Pyritic	Sulfate	Organic	Ash	Volatiles	Fixed Carbon	Heat Content Btu/lb
Appalachian Coal Basin	Sewickley Meigs Creek No. 9	Penn Ohio	Warwick Muskingum	hVAb	1.50	1.37	1.09	0.01	0.27	40.47	27.77	31.76	8612
				hVAb	3.36	6.08	3.65	0.06	2.37	21.68	36.36	41.96	11014
	Pittsburgh	Penn	Mathies	hVAb	1.67	1.46	1.05	0.04	0.37	41.01	24.53	34.46	8154
	Pittsburgh W. Va.		Humphrey No. 7	hVAb	1.63	2.58	1.59	0.01	0.98	9.88	37.66	52.46	13631
	Pitts. No. 8	Ohio	Egypt Valley No. 21	hVAb	2.07	6.55	5.07	0.14	1.34	25.29	36.12	38.59	10594
	Pitts. No. 8	Ohio	Powhatan No. 4	hVAb	2.10	4.12	2.57	0.19	1.36	37.17	29.01	33.82	8603
	U. Freeport	Penn	DeImont	hVAb	0.77	4.89	4.56	0.08	0.25	27.18	28.33	44.49	11012
	U. Freeport	Penn	Jane	hVAb	1.17	1.85	1.44	0.00	0.41	21.75	30.07	48.18	11932
	Freeport	Penn	Marion	hVAb	2.21	1.37	0.90	0.02	0.45	26.40	25.45	48.15	11046
	Middle Kittanning Lower	Penn	Lucas	hVAb	3.89	1.79	1.42	0.05	0.32	8.68	35.30	56.02	13451
Eastern & Western Interior Coal Basins	Lower Kittanning	Penn	Bird No. 3	lvb	0.84	3.14	2.87	0.05	0.22	30.23	16.18	53.59	10550
	Lower Kittanning	Penn	Fox	hVAb	1.82	3.82	3.14	0.04	0.64	13.55	38.33	48.12	12973
	Kittanning Clarion 4A	Ohio	Meiggs	hVAb	4.77	3.73	2.19	0.06	1.48	26.53	34.92	38.55	10246
	Mason	E. Kentucky	No. 1 ^b	hVAb	2.22	3.12	1.98	0.08	1.06	11.39	38.91	40.70	13054
	Illinois No. 5	Illinois	Eagle No. 2	hVAb	3.31	4.29	2.64	0.04	1.61	26.53	34.30	39.17	10566
	No. 9	W. Kentucky	Camp No. 1 & 2	hVAb	3.99	4.51	2.80	0.06	1.65	21.13	35.86	43.01	11105
	Herrin No. 6	Illinois	Orient No. 6	hVAb	3.51	1.66	1.30	0.01	0.36	22.51	31.67	45.82	11163
	Des Moines No. 1	Iowa	Meldon	hVAb	13.29	6.39	5.24	0.15	1.00	15.74	40.62	43.64	11760
	Rosebud	Montana	Colstrip	subA	20.41	1.01	0.34	0.00	0.67	10.38	43.09	46.53	11591

^aAll values are the average of triplicate determinations.
^bDixie Fuel Company.

Because of the widespread application of physical cleaning techniques for removal of non-combustible rock (which includes varying amounts of pyrite) from coal (along with some carbon), float-sink fractionation was performed to define the relative utility for each coal of washing and chemical desulfurization. The summary chart (Table 2) of pyritic sulfur removal results shows that a) the Meyers' Process, at its current state of development, removes 83-98% of the pyritic sulfur content of the 19 coals studied, resulting in total sulfur content reductions of 40 to 82%, b) nine of the coals are reduced in sulfur content to the 0.6 - 0.9% sulfur levels generally consistent with the federal standard for new stationary sources and many state standards, while two coals are reduced below 1.0% sulfur by physical cleaning, c) with the exception of the Jane and Lucas mines, the Meyers' Process removes significant to very large increments of sulfur over that separable by physical cleaning, and d) in one case, the Mathies mine, coal cleaning results in a sulfur content increase.

State emission regulations for discharge of sulfur oxides from utility and large industrial power plants⁽⁵⁾ can also be met by application of the Meyers' Process. The Pennsylvania state standard for eight air basins is approximately 1.1% sulfur, for coal of 25mm btu/ton. The Marion, Mathies, Bird No.3 and Delmont mines all meet this standard after chemical desulfurization but do not meet the standard after efficient physical cleaning. These coals could also be transported to New Jersey or New York to meet their state standards of approximately 1.0%, and 1.8 and 2.4% sulfur, respectively. The Meigs and Powhatan No.4 mines would meet the '28 county standards' of approximately 2% sulfur for the state of Ohio after treatment by the Meyers' Process, whereas efficient cleaning of these coals reduces their sulfur content to only 2.8 and 3.3%.

The Camp mine in western Kentucky meets the state standard for 'Priority 3' regions of less than 2.3% sulfur after treatment by the Meyers' Process, whereas physical cleaning reduces the total content of this coal to 2.9%. The Humphrey No.7 mine is reduced to 1.5% sulfur, which meets the West Virginia standards for 'Regions 2 and 3' of 1.7 and 2% respectively, whereas physical cleaning reduces the sulfur content to 1.9%. The Weldon mine in Iowa is reduced to 2.3% sulfur by the Meyers' Process which meets the state requirement of approximately 3.1% sulfur. Physical cleaning does not meet the standard, reducing the sulfur content to 3.8%.

We feel that process improvements such as more efficient residual sulfur and sulfate removal and especially utilization of physically cleaned coal will cause most coals to be further reduced in sulfur content to the '95% removal' level shown in Column 4 of Table 2.

In commercial practice for production of clean fuel, it is very likely that an optimum process cost and product will be obtained by cleaning coal prior to ferric sulfate leaching, to remove rock and some of the larger pyrite particles. There are preliminary indications that the efficiency of the Meyers' Process may be enhanced by utilization of physically cleaned coal.

TABLE 2
SUMMARY OF PYRITE REMOVAL RESULTS
COAL SURVEY PROGRAM

Mine	% Total Sulfur w/w in Coal ^{a,b}			Meyers Process Pyrite Conversion % w/w	Meyers Process Total Sulfur Decrease % w/w	% Sulfur in Coal ^d After Efficient Coal Cleaning
	Initial	After Meyers' Process				
		Current Results	95% Removal ^c At			
1. Colstrip	1.0	0.7	0.7	83	40	e
2. Warwick	1.4	0.8	0.3	92	43	1.0
3. Marion	1.4	0.7	0.5	94	50	1.2
4. Mathies	1.5	0.9	0.5	98	44	1.7
5. Jane	1.8	0.7	0.5	91	61	0.8
6. Orient No.6	1.7	0.9	0.4	96	47	1.4
7. Lucas	1.8	0.9	0.4	92	50	0.7
8. Humphrey No.7	2.6	1.5	1.1	91	42	1.9
9. No. 1	3.1	1.6	1.2	90	48	2.3
10. Bird No. 3	3.1	0.8	0.4	95	74	1.5
11. Fox	3.8	1.6	0.8	89	58	2.0
12. Meiggs	3.7	1.9	1.6	93	49	2.8
13. Powhatan No.4	4.1	2.0	1.7	84	51	3.3
14. Camp	4.5	2.0	1.8	96	56	2.9
15. Eagle No. 2	4.3	2.0	1.8	94	51	2.9
16. Delmont	4.9	0.9	0.6	98	82	2.1
17. Muskingum	6.1	3.2	2.6	93	48	4.4
18. Egypt Valley	6.6	2.7	1.7	93	49	4.6
19. Weldon	6.4	2.2	1.4	98	66	3.9

^aDry, moisture-free basis.

^bExperimental conditions are shown in the Experimental Section. ^d1.90 float material, 14x0 mesh is defined here as the limit of efficient coal cleaning.

^cSulfur content of coal at 95% pyrite removal, and no increase in sulfate or measured organic sulfur content.

^eFloat-sink testing was not run on this coal due to its low ash and pyrite content.

A more detailed coal analysis summary for coals tested by the Meyers' Process is shown in Table 3. These results show that a) a measured heat content rise of up to 5 - 10% is obtained for the Appalachian and some of the Interior Basin coals, while on a dry mineral matter and pyrite heat content free basis, heat content changes are essentially negligible as to be expected for negligible reaction of the coal organic matter, b) the Colstrip (western) and Orient No.6 (eastern interior) coals show small heat content losses, c) ash removal, in addition to that accounted for by pyrite decrease was observed in varying degrees for all coals, d) an increase in organic sulfur content in excess of that for ash removal occurs for some coals while small decreases occur for others.

As the Appalachian Basin provides most of the US coking coal production, it was deemed desirable to obtain free swelling index (FSI) data on these coals. Actual coke-oven testing is, of course, required to obtain assurance of retention of coking properties after Meyers' Process treatment. FSI values of 4 - 8 measured for the Appalachian coals showed no significant change after processing.

EXPERIMENTAL METHOD

Chemical Removal of Pyritic Sulfur.

The general conditions for pyritic sulfur removal have been adapted from the bench-scale studies⁽⁴⁾ with the objective of obtaining 90% - 100% pyritic sulfur removal and of simulating process design as nearly as possible, consistent with efficient laboratory operations.

Mesh Size - coal ground to 100 mesh x 0 or finer has been found to give high extraction rates and to be most satisfactory for laboratory scale sampling, although coal top sizes up to -1/4" have been tested and give reasonable although reduced reaction rates.

Ferric Ion Concentration - ferric sulfate solution 1N in ferric ion appears to be optimum, although differences due to concentration change do not appear to be great.

Reaction Temperature - the reaction temperature was held at the reflux temperature of 1N ferric sulfate solution which is approximately 102°C. This allows a reasonably high reaction rate and yet does not require pressure equipment.

Reaction Time - each coal was leached a total of 10 - 24 hours depending on the characteristics of the individual coal being treated.

Ferric Ion to Total Iron Ratio⁽⁴⁾ - since the rate of pyrite removal is slowed substantially by ferrous ion accumulation (see eq 3), each coal was treated under conditions designed to keep $\bar{Y} > 0.80$ by one of the following means:

TABLE 3
TREATED COAL ANALYSIS SUMMARY^a

Region	Seam	Mine	Dry Forms of Sulfur, % w/w					Dry Proximate Analysis, % w/w				
			Total	Pyritic	Sulfate	Organic	% Pyrite ^b Removal	Ash	Volatiles	Fixed Carbon	Heat Content btu/lb	Content Change %
Appalachian Coal Basin	Sewickley Meigs Creek No. 9	Warwick Muskingum	0.82 3.22	0.09 0.27	0.14 0.17	0.59 2.78	92 93	35.32 16.05	26.61 36.95	38.07 47.00	9365 11587	8.7 5.2
	Pittsburgh Pittsburgh Pitts. No. 8	Mathies Humphrey No. 7 Egypt Valley No. 21	0.94 1.49 2.71	0.02 0.14 0.38	0.10 0.10 0.13	0.82 1.25 2.20	98 91 93	36.43 6.97 18.69	25.51 37.04 38.08	38.05 55.93 43.23	9024 13949 11533	10.7 2.3 8.9
	Pitts. No. 8	Powhatan No. 4	2.04	0.43	0.12	1.49	84	32.12	29.28	36.60	9430	9.6
	U. Freeport J. Freeport Freeport	Delmonta Jane Marion	0.90 0.69 0.68	0.11 0.14 0.05	0.05 0.06 0.06	0.74 0.49 0.57	98 91 94	20.14 17.99 22.62	29.95 30.36 25.31	49.91 51.65 52.07	12150 12417 11720	10.3 4.1 6.1
	Middle Kittanning Lower	Lucas	0.89	0.20	0.12	0.57	92	6.32	35.15	58.53	13883	3.2
	Kittanning Lower	Bird No. 3	0.80	0.16	0.11	0.53	95	24.17	17.57	58.25	11493	8.9
	Kittanning Clarion 4A	Fox Meigs	1.64 1.94	0.37 0.16	0.09 0.14	1.18 1.64	89 93	9.72 20.39	38.31 35.27	51.97 44.34	13174 10582	1.5 3.3
	Haron	No. 1	1.62	0.21	0.09	1.32	90	8.50	37.63	53.87	13341	2.2
	Illinois No. 5	Eagle No. 2	2.04	0.19	0.23	1.62	94	19.49	34.62	45.89	11428	6.5
	Western Interior Coal Basins	No. 9 Herrin No. 6 Des Moines No. 1	Camp No. 162 Orient No. 6 Weldon	2.02 0.93 2.25	0.14 0.06 0.15	0.16 0.17 0.12	1.72 0.73 1.98	96 96 98	15.27 18.25 5.94	36.45 31.92 -	48.28 48.83 -	11740 11034 12735
Western	Rosebud	Colstrip	0.69	0.06	0.06	0.57	83	5.17	42.45	52.38	11321	2.3

^aAll values are the average of duplicate or triplicate runs.

^bBased on before-and-after weight of pyrite present.

- Increasing the solvent to coal ratio (w/v) from a nominal 10 to a maximum of 40
- Changing the leach solution after 3 - 6 hours of reaction or more often if required
- A combination of the above.

Post Sample Treatment - after treatment, the samples were thoroughly washed to remove any residual leach solution and then dried. All sample calculations were done on a dry basis in order to eliminate variables due to wetness of the coal. Sulfur forms and proximate analysis have been obtained for each treated coal sample.

The exact procedure is described below:

One hundred grams of 100 mesh x 0 coal were added to 2-l refluxing 1N ferric sulfate solution contained in a 4-necked 3-l glass cylindrical reaction vessel equipped with a mechanical stirrer, reflux condenser and a thermocouple attached to a recorder. Each vessel also had a stopcock at the bottom for taking samples and was heated by a specially constructed heating mantle. After the coal addition, an additional 0.5-l 1N ferric sulfate solution was used to wash down the sides of the vessel. At this point, the t_0 solution sample was taken and the leaching process was considered started. Then, the reaction mixture, which was at $88 \pm 4^\circ\text{C}$, was rapidly brought to reflux, a process that takes 8 - 12 minutes. Leach solution samples for each iron analysis were taken by drawing a 200 ml aliquot of the reaction mixture from which a 20 ml sample was taken and cooled immediately to 0°C . Unused material was returned to the reaction flask. After cooling, a 14 ml aliquot was centrifuged to remove all suspended solids and 10 ml of this was used for iron analysis. Any remaining coal or leach solution was returned to the reaction flask.

After 4 - 6 hours when Y was reduced to approximately 0.8, the heating was stopped and the reaction mixture was drained from the flask, filtered and sucked as dry as possible. The final reaction volume and approximate solvent retention on the coal were then determined. The wet, unwashed coal was then slurried with 200 ml fresh ferric sulfate solution at 30°C and added to 2-l fresh 1N ferric sulfate solution at reflux. Another 300 ml ferric sulfate was used to wash any residual coal into the flask. A t_0 leach solution sample was taken immediately and the entire reaction mixture was brought to reflux in 8 - 12 minutes. Leach solution samples were taken at regular intervals, and after a total elapsed reaction time of 10 to 24 hours, the reaction mixture was drained from the reaction flask, filtered and washed clear with 0.5-0.1-l water.

The extracted coal was slurried with 2-l of water or 1N sulfuric acid of $\sim 80^{\circ}\text{C}$ for 2 hours, filtered and then stirred with another 2-l at $\sim 80^{\circ}\text{C}$ for an additional two hours. After filtration, this procedure was repeated with 2-l water at $\sim 80^{\circ}\text{C}$. If scheduling did not permit coal to be extracted with toluene immediately, it was stirred at $\sim 50^{\circ}\text{C}$ for an extended period until it would be filtered and extracted.

After the extraction of residual sulfate and iron, the wet coal was transferred into a 1-l round bottom flask equipped with a mechanical stirrer and Dean-Stark trap. Then 400 ml toluene was added and the mixture was brought to reflux. This was continued until all the water was azeotroped off (approximately 0.75 - 1.25-hr and 50 - 75 ml) plus another 15 minutes. The hot solution was then filtered, washed with 50 - 75 ml toluene, and then dried in a vacuum oven at 100 - 120°C . This coal was then weighed and analyzed.

FLOAT-SINK TESTING (Commercial Testing & Engineering Co.)

Five hundred pounds each of the 1-1/2" x 100 mesh, 3/8" x 100 mesh and 14 mesh x 0 portions obtained from the initial sampling of the coals were fractionated according to standard float-sink procedures using organic liquids of 1.30, 1.40, 1.60 and 1.90 specific gravities. Head samples for each size (or grind), each gravity portion and the two 100 mesh x 0 samples were analyzed on a dry basis for % w/w ash, total sulfur and pyritic sulfur. The raw data was then used to calculate washability data showing cumulative recovery and cumulative reject at the various specific gravities for each of the size portions.

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The Meyers' Process is a new and potentially low-cost approach for removing pyritic sulfur from coal which utilizes a simple ferric sulfate leaching technique. The pyritic sulfur content of coal is converted to elemental sulfur and iron sulfates which become process products. Ferric sulfate is regenerated by reaction with oxygen or air. Bench-scale data and process design studies indicate that the process may be designed utilizing a number of alternative processing methods. Some of the parameters which have been tested and considered include the following: air vs oxygen for regeneration, coal top sizes from 1/4-inch to 100 mesh, leaching and regeneration temperatures of 50°C up to 130°C, concurrent leaching and regeneration in the same vessel and recovery of elemental sulfur by either solvent extraction or vaporization. Coal treatment plants, based on the process, may be constructed utilizing standard equipment such as leaching vessels, thickeners, vacuum filters, etc., and standard materials of construction such as stainless steel, rubber-lined equipment and the like. The simplicity of the process and the mild conditions utilized indicate that desulfurization costs may well be favorable when compared with alternative sulfur oxide control methods.

COAL DESULFURIZATION: COSTS/PROCESSES AND RECOMMENDATIONS,

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This paper contains a review of the costs and technology for removal of sulfur by physical and chemical means. In particular, experimental results and economic analyses are presented for the use of $\text{Fe}_2(\text{SO}_4)_3$ to remove pyritic sulfur. Also, included is a description of Kennecott Copper's new low temperature process for the removal of pyrite and some organic sulfur from coal. The major conclusions briefly stated are:

- (1) The best physical desulfurization process can only remove about 70% of the pyrite and has costs in the neighborhood of stack gas cleaning.
- (2) While $\text{Fe}_2(\text{SO}_4)_3$ does remove more than 95% of the pyrite, the reaction time is in the order of hours which leads to high capital and operating costs. In addition, the regeneration of ferric ion remains a major process uncertainty.
- (3) Kennecott's process has removed 100% of the pyritic sulfur and 20% of the organic sulfur in Illinois No. 6 coal at costs comparable to stack gas cleaning.

COAL DESULFURIZATION BY MAGNETIC FORCES

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INTRODUCTION

Magnetic cleaning of coals has been studied in the past¹ by passing coal particles - usually pre-treated - suspended in air streams through conventional magnetic separators. The work reported here² is a systematic attempt at using high gradient magnetic separation techniques in coal slurries³.

OBJECTIVES

There is a worldwide demand for new coal cleaning processes. This demand stems from the following: (i) upgrading of local coal reserves, mainly in developing countries; (ii) air pollution abatement, mostly of SO_2 and fly ash, in developed countries (the U.S. in particular); and (iii) preparation of raw materials for coal gasification and liquefaction, mainly in the United States. In response to this demand the work described here was conducted with the following objectives:

(i) Determine the technical and economic feasibility of using magnetic technology in coal cleaning. Brazilian coal from the Sideropolis field (30% mineral matter and 2-3% sulfur mainly pyritic) was used as a case example.

(ii) Study the fundamental principles of magnetic separation.

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PRINCIPLES OF MAGNETIC DESULFURIZATION OF COAL SLURRIES

The rationale for magnetic removal of minerals from coal is based on the magnetic susceptibility of its components. In 10^{-6} CGS units, the values are: organic material, -0.4 to -0.8; shales, 39 to 45; kaolins, 20 to 39; sulfides, 0.3 to 120; carbonates, -0.4 to 100; chlorides, -0.9 to -1.3; accessory minerals, of minor importance, -1.2 to 20. These values indicate a limitation on the removable amounts, for not all of the minerals are paramagnetic. Unfortunately, in many coals the minerals are intimately mixed with the coal substance, and grinding to fine sizes is the required prior to separation in order to maximize differences in magnetic susceptibility. In coal cleaning we are usually dealing with the removal of paramagnetics (pyrites and a fraction of the other minerals) from the coal matter (largely diamagnetic).

The translational force - attractive or repulsive - along a given direction on a small particle of a non-ferromagnetic material immersed in a magnetic field is given by

$$F_m = \chi \cdot V \cdot H (dH/dx) \quad (1)$$

where F_m is the magnetic force acting on the particle in the x direction,

χ is the volume susceptibility of the particle, V is the particle volume, χV is magnetization, and H is the total magnetic field acting on the particle in the x direction. The relatively recent availability of much larger magnetic fields and field gradients has permitted extension of use of magnetic separation beyond highly magnetic materials, i.e., ferromagnetics, to mixtures of paramagnetic and diamagnetic substances.

The basic principle of magnetic separation is then the development of a magnetic force - attractive or repulsive - as particles with different

susceptibilities enter the reach of a magnetic field. Depending upon the geometry and the design of the separator, and the nature of the medium carrying the particles to be separated, forces arise - particle weight, buoyancy, and drag by the fluid carrying the particles, etc. - which oppose the separation

Inspection of Equation 1 suggests the important magnetic characteristics which a separator design should provide, namely an intense field strength and a large field gradient. Both should cover the largest possible volume to increase the capacity of the separator.

Consider a separator which consists of a packed column, inserted vertically in the bore of a solenoid magnet. The packing, a filamentary ferromagnetic material (stainless steel wool or a steel wire screen), is the source of the field gradient and holds magnetically captured particles. Our simplified model considers an isolated strand of steel wool taken as a cylindrical wire of uniform cross section (e.g. 100 μ in diameter), inserted horizontally in a volume (e.g. the bore of a Bitter solenoid magnet), where the magnet field is uniformly vertical. The pyrite particles - ranging in size from 0 to 600 μ - are carried in the water slurry flowing past the strand. The capture of a pyrite particle by the strand depends on the ratio R of the magnetic force to the opposing forces (net weight, W, and the hydrodynamic drag force, F_d) acting on the particle :

$$R = \frac{F_m}{W + F_d} = \frac{\chi V H (dh/dx)}{W + F_d} \quad (2)$$

The expression for the magnetic force depends on the applied field, the magnetic properties of the materials, and the system geometry. It is, in all cases, a function of the center-to-center distance between the particle and the magnetized strand, and of the angular position of the particle

with respect to the strand. The expression for F_d varies with the flow regime, i.e. with the particle Reynolds number, and also with the particle shape. The net weight depends on the volume of the particle, its density and the density of the liquid.

A mathematical model based on the above forces was developed to simulate the effect of the principal independent variables on the probability of capture of mineral particles, as measured by the value of R . The magnetic field was 20 kOe, the source of field gradient was a cylindrical steel strand of 100 microns in diameter, and only pyrite particles (susceptibility equal to 25×10^{-6} emu/gm) were considered.

Figure 1 shows the effect of particle size on R for different slurry velocities (V_s). The curves indicate that there is an optimum particle size for which the probability of capture reaches a maximum. The effect of the slurry velocity is shown by the flattening of the curves as the velocity increases. In all cases the drag force predominates over the magnetic force for small particles where the particle weight is negligible. For large sizes the net weight is the most important force. For intermediate sizes the magnetic force is relatively more important.

APPARATUS AND PROCEDURES

The schematic of the apparatus used in this work is shown in Figure 2 and described elsewhere³. Pre-washed coal - 25.4 to 0.6 mm top size - was ground to 0.42 to 0.044 mm top size. Slurries were prepared by mixing known amounts of coal, of known size distribution, water, and for the finer sizes, a wetting agent. The slurry was passed once through the separator, essentially a packed column inserted in the bore of a solenoid magnet. The packing consisted of magnetic stainless steel wool or screens at packing densities

ranging between 1 and 13 volume percent. The materials retained (mags), and the materials passed through (tails) were analyzed for total ash content and sulfur. Organic sulfur was estimated by the differences between total sulfur and pyritic plus sulfate sulfur. In a few cases the magnetization of the coal minerals in the original coal, tails and mags were measured. Recoveries (total, ash, sulfur, etc.) are always defined with respect to the total amounts present in the original coal.

EXPERIMENTAL RESULTS

Evidence of Magnetic Separation

The magnetization curves of the coal minerals in the products of magnetic separation provide evidence of magnetic action. The coal minerals were obtained by low temperature ashing (LTA), in which the coal substance is slowly combusted at 150 C, leaving behind the unaltered minerals⁴. The measurements employed Foner's vibrating-sample magnetometer⁵. As shown in Figure 3 at a field of 15 kOe the magnetization of the LTA of the "tails" is 30 times smaller than the LTA of the "mags", indicating the removal of minerals with higher susceptibility from the original coal and their concentration in the "mags".

Typical Result

A typical result of a laboratory test of magnetic separation of coal is shown below. The void volume of the packing was 95%, the field intensity was 20 kOe, the slurry concentration was 2.5%, the top particle size was 44 microns and the slurry velocity was 2.0 cm/sec. The recovered product constituted 80% of the feed and contained only 0.81% sulfur as opposed to 1.32% sulfur in the feed. In a practical situation the "mags" could be further processed to improve the product yield.

FEED	BASE	= 100	
		27. %	Ash
		1.32 %	Total Sulfur
		0.66 %	Pyritic Sulfur
TAILS	RECOVERY	= 80.8	
		24. %	Ash
		0.81 %	Total Sulfur
		0.24 %	Pyritic Sulfur
MAGS	RECOVERY	= 14.4	
		38.9 %	Ash
		2.52 %	Total Sulfur
		2.01 %	Pyritic Sulfur

Effect of the Independent Variables

The experimental results confirmed the force balance model with respect to the effects of particle size and slurry velocity. One of the important predictions of the model is that there should be a given particle size for which R reaches a maximum. Consequently we would expect that the sulfur concentration, and the sulfur recovery in the mags would peak at the same diameter, if pyrites are the dominant form of sulfur, and if they are sufficiently liberated.

In a series of runs coal was sieved to produce narrow particle size distributions which gave approximately monodisperse slurries when suspended in water. The following size ranges were obtained: (i) below 44μ , (ii) $44-53\mu$, (iii) $53-63\mu$, (iv) $63-74\mu$, (v) $74-105\mu$, (vi) $105-177\mu$, and (vii) $177-420\mu$. Steel screens were used as packing (91% void). The slurry concentration was 2.6 gm/100 ml and the linear velocity ranged between 2.3 and 2.6 cm/sec. The applied magnetic field was kept constant at 20 kOe. Figure 4 shows the effect of particle size on sulfur recovery in mags.

Analysis of the forms of sulfur for the maximum point showed that pyritic sulfur accounted for most of the total sulfur in mags.

According to the model, R should decrease as the slurry velocity increases. Consequently "mags" recovery should decrease, sulfur concentration in the mags should increase because the particles of higher susceptibility (pyrites) should constitute a majority of those retained. All these predictions were confirmed experimentally.

ECONOMIC ANALYSIS

A practical scheme of magnetic separation applied to coal beneficiation would be based upon the same concepts described here but the operation would be carried out in large capacity continuous equipment. In one possible situation the separator packing would move in and out of a magnetic field region to allow for continuous washing of the packing to remove trapped materials. The slurry fed to the separator would always find a clean packing. A continuous device of this type has been developed for use in beneficiating taconite ore which resembles, geometrically, a 'carousel' slide projector.

Table 1 summarizes the results of a preliminary economic analysis of a magnetic separator for coal cleaning, based on experimental results. Top particle size was 28 mesh, field intensity was 20 kOe and slurry velocity was 4.0 cm/sec in a once through operation. We tested the sensitivity of the processing costs to changes in the cost of power, depreciation time, etc. The estimated processing costs fell into a range of 30 to 63 cents per ton of coal produced. This range compares favorably with conventional beneficiation techniques.

TABLE I

COSTS OF MAGNETIC DESULFURIZATION OF COALS

Typical Case

field 20 kOe
 size distribution 28 mesh x 0
 once through operation

<u>Feed</u> (=100)	<u>Product (tails)</u> (=72)
Ash % 30.1	27.9
Sulfur % 1.80	1.80

Plant Characteristics

	<u>Base Case</u>	<u>Alternatives</u>
Investment, 10^3 \$	6480	6480 - 12960
Operational Capacity, 10^3 t/yr	7920	2640 - 7920
Number of units (3.6 m^2 each)	8	8 - 16
Depreciation time, yrs	20	10 - 20
Power costs, mills/kwhr	10	10 - 20

Processing Costs, cents/ton coal FOB Plant

	<u>Base Case</u>	<u>Alternatives</u>
Indirect Costs	9.2	9.2 - 27.9
Direct Costs	12.5	12.5 - 18.9
Total Costs		
Coal Fed	21.7	25.8 - 45.5
Coal Produced	30.1	35.8 - 63.2

CONCLUSIONS AND RECOMMENDATIONS

The principal conclusions of this study are summarized below.

- The magnetic cleaning of coals can remove practically all the liberated pyritic sulfur and a portion of the other minerals.
- The experimental results can be predicted or interpreted, at least qualitatively, by the proposed model.
- The experimental work has confirmed the importance of the key independent variables: particle size and liberation; slurry velocity; field intensity and packing characteristics.

With regard to the process economics, the following points are important:

- magnetic separation is a capital intensive operation;
- without superconducting magnets the operation is sensitive to the cost of power;
- grinding costs were not included because, although fine grinding increases liberation, the probability of magnetic capture is diminished, according to the model;
- the process looks commercially feasible.

Recommendations for future research include:

- enhancement of the susceptibility of the materials to be separated, probably by changes in the nature of the particle surface;
- study of additional coals to characterize their behavior;
- study of the capacity and performance of systems of separators with mags recycle;
- coupling of magnetic separation with conventional coal cleaning schemes;
- use of air laden with coal;
- fundamental studies including:
 - magnetic separation visualization
 - use of systems simpler than coal slurries

- magneto-chemistry of the pyrite system
- quantitative modelling, i.e. development of a magnetic adsorption theory

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CAPTIONS TO ILLUSTRATIONS

- Figure 1. Effect of particle size and slurry velocity on ratio of magnetic force to drag force plus net particle weight as indicated by simple model (slurry velocity, cm/sec: (a) 0.1; (b) 1.0; (c) 2.0)
- Figure 2. Schematic Arrangement of Equipment
- Figure 3. Observed effect of magnetic field on magnetization (m, mags; f, feed; t, tails)
- Figure 4. Observed effect of particle size on sulfur recovery in mags

